logical ion transport mechanism may in part be due to the complexation properties of the macrocyclic carrier molecules.

The central cavities of valinomycin and monactin are considerably larger (36 and 32 ring atoms, respectively) than that for I (18 ring atoms), yet they show preferences for cations of the same size as indicated by similar stability[13] and permeability[4,5] sequences. It would thus appear that these larger molecules possess considerable flexibility in order to be able to assume that orientation about the metal ion which is required for maximum complex stability. Such conformational differences between the noncomplexed and complexed ligands have been demonstrated by several workers.[11,12,21] The efficiency and high ion selectivity of the complexation reactions in the antibiotics appear to be determined by the possible conformational states of these compounds.[12] Nuclear magnetic resonance data in the case of nonactin indicate that complexation is accompanied by changes in the dihedral angles between adjacent hydrogens which are sufficient to account for the necessary changes in the diameter of the central cavity required to fit the metal ion.[26]

The macrocyclic ligands discussed here have interest not only from the standpoint of their application as model carriers in investigations of ion transport processes, but also in selective coordination chemistry and in ion selective resins and electrodes. The possible range of complexation properties and individual specificities of macrocyclic compounds has recently been greatly extended through the introduction of nitrogen and sulfur atoms into the macrocyclic rings,[27,28] and the preparation of analogs of the cyclic polyethers containing bridgehead nitrogen atoms.[29] Synthesis of these new macrocyclic ligands opens a new area of coordination chemistry with wide application in biological, industrial, and analytical fields.

Acknowledgments. We appreciate many helpful discussions with Dr. H. K. Frensdorff, Mr. C. J. Pedersen, and Dr. John O. Hill.

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(26) J. H. Prestegard and S. I. Chan, *Biochemistry*, **8**, 3921 (1969).

(27) L. H. Lindoy and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4690 (1969).

(28) S. C. Cummings and R. E. Sievers, *ibid.*, **92**, 215 (1970).

(29) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969).

Photochemical Reactions of Copper(II)-1,3-Diketonate Complexes[1]

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Abstract: When alcohol solutions of bis(1,3-diketonate)copper(II) are exposed to 254-nm radiation the copper(II) ions are reduced to metallic copper. The photochemistry of five copper chelates was studied as a function of irradiating wavelength, light intensity, and chelate concentration. On this basis, the primary photochemical process was determined to be a reduction of Cu(I1) to Cu(I) followed by a thermal reduction of Cu(I) to copper metal. The quantum yield was found to be a function of the ligand ionization potential. Mechanisms are proposed and discussed.

In recent years a number of photochemical studies involving coordination compounds have been published.[2] However, as yet there is little quantitative information about reactions that take place during irradiation of charge-transfer bands. We have chosen the 1,3-diketonate chelates to study these reactions for several reasons; both metal-to-ligand and ligand-to-metal charge-transfer absorptions are present in the spectra, the energies of the charge-transfer bands may be systematically varied by changing the metal ion and the chelate ring substituents, and a large amount of absorption and emission spectral data is available in the literature. To date only two quantitative studies on the photochemistry of 1,3-diketonate chelates have appeared.[3,4] These papers deal with Co(III) and Fe(III) 1,3-diketonates. The work presented herein is part of our continuing research on photochemically induced redox reactions of metal chelates.

Very few photochemical studies on the coordination complexes of copper have been undertaken. In 1966, Shagisultanova[5,6] reported the photoreduction of Cu(II) chelates of ethylenediamine, oxalate, and glycinate. The reduction observed was from Cu(II) to Cu(I). However, in preliminary irradiations of bis(1,3-diketonate)copper(II) chelates we observed complete reduction in alcoholic solvents to metallic copper. The Cu(II) ions reduced in this manner produce a lustrous metallic mirror on the irradiated cell face. This work was begun to study these photoinduced redox reactions with several bis(1,3-diketonato)copper(II) chelates.

The ultraviolet absorption spectra of bis(1,3-diketonato)copper(II) have been studied and the transitions assigned.[7,8] The spectra in this region consist of two

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(1) Presented in part at the 11th International Conference on Coordination Chemistry, Haifa, Israel, Sept 1968.

(2) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

(3) N. Filipescu and H. Way, *Inorg. Chem.*, **8**, 1863 (1969).

(4) H. D. Gafney and R. L. Lintvedt, *ibid.*, **9**, 1728 (1970).

(5) G. A. Shagisultanova, *Russ. J. Inorg. Chem.*, **11**, 510 (1966).

(6) G. A. Shagisultanova and L. A. Ill'yikevitch, *Zh. Neorg. Khim.*, **11**, 945 (1966).

(7) J. P. Fackler, F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963), and references therein.

separate bands. The first at 280–310 nm has been assigned to a $\pi \rightarrow \pi^*$ transition within the ligand while the second band at *ca.* 230–255 nm has been assigned to a charge-transfer transition of the ligand-to-metal type. Evidence presented in this paper supports the assignment of the 230–255-nm band to a ligand-to-metal charge-transfer transition.

Experimental Section

Preparation of Compounds. The 1,3-diones were obtained from commercial sources. The complexes were prepared by standard methods[9,10] and were purified by recrystallization. The chelates studied and the abbreviations used throughout this paper are: bis(2,4-pentanedionato)copper(II), Cu(acac)$_2$; bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II), Cu(tfac)$_2$; bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), Cu(hfac)$_2$; bis(5,5-dimethyl-2,4-hexanedionato)copper(II), Cu(t-buac)$_2$; and bis(1-phenyl-1,3-butanedionato)copper(II), Cu(bzac)$_2$. The Cu(hfac)$_2$ was dried according to the method of Bertrand and Kaplan.[11] The resulting green-violet crystals melted at 93°.

All solvents used in the studies were reagent grade and distilled prior to use.

The electronic absorption spectra were recorded using a Cary 14 spectrophotometer. Optical density measurements were made with a Beckman DU spectrophotometer and calibrated quartz cells. This instrument was calibrated with a mercury arc. Infrared spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer. The atomic absorption measurements were recorded on a Beckman Model 1301 atomic absorption accessory equipped with a DB-G spectrophotometer.

The analytical procedure followed in determining the amount of plated copper metal was to rinse a freshly deposited film a number of times with distilled absolute ethanol. The copper was then dissolved in 1 ml of a distilled mixture (boiling point 115–119°) of 68% HNO$_3$ and conductivity water. This was then transferred quantitatively to a 5-ml volumetric flask and diluted to volume with conductivity water. The absorbance of these solutions was determined without further dilution at 324 nm by atomic absorption spectrophotometry. The number of moles of copper was determined by comparison to a plot of absorbance of standard solutions of known copper concentration. The absorbances of the standards and the samples were corrected for a slight absorption due to the acid.

Preliminary experiments were carried out in a reaction vessel equipped with a quartz immersion well. The source was an unfiltered Hanovia medium-pressure Hg lamp with a 450-W transformer. The photolysis vessel was connected to a vacuum line and a trap at 77°K. The trap could be shut off and removed for product analysis. A second type of reaction cell contained an opening in which a conductivity cell was mounted at right angles and adjacent to the immersion well. Resistance measurements were made during the photolysis using an Industrial Instruments Model RC16B2 conductivity bridge and a nonaqueous conductivity cell (cell constant is 0.092 cm^{-1}).

For quantum yield determinations the source was a low-pressure Klockner-Moeller Original Hanau-Type P1-368 Hg lamp which emitted approximately 90% of its output at 2537 Å. The lamp was connected to a Raytheon voltage stabilizer with a 115-V output at 17.4 A. The lamp was contained in a 19 cm × 6.5 cm diameter cylindrical housing with a 5 cm × 2 cm opening. The housing was equipped with two gas jets through which dry nitrogen was passed during operation. By varying the current and voltage through a variable transformer in series with the lamp and by varying the nitrogen flow an eightfold variation in light intensity could be obtained.

The cell was a 10 mm × 10 mm × 45 mm rectangular fused quartz cell equipped with a 14/20 ground-glass joint. The cell was connected to an upper section which had a side arm and vacuum stopcock. This made it possible to connect the cell to a vacuum line for degassing the solutions. The solutions were frozen by immersion in liquid nitrogen and degassed by repeated freeze–pump–thaw cycles. The cell was mounted 2 cm from the lamp housing in a brass constant-temperature block. The block was constructed so that the entire cell face could be exposed to light. For photolysis at lower temperatures the full cell was precooled to the desired temperature before placing it in the brass block. At low temperatures, the solution temperature was on the average 3.2° above the block temperature. The solutions were stirred during the photolysis with 5-mm magnetic stirring bars.

Quantum Yield Determinations. The general procedure was to determine the quantum yield of decomposition of the chelate by measuring the amount of chelate that had decomposed at a constant light intensity in a known time. The light intensity was determined by ferric oxalate actinometry.[12–14] After the lamp and N$_2$ flow were turned on and allowed to warm up for 2 hr, the light intensity was determined by irradiating a 0.009 *M* ferric oxalate solution. The light intensity was measured before and after the photolysis. An average value was used in the calculation of quantum yields. The intensity variation was always less than 5% except when the lamp was run at a lower voltage, in which case the variation was less than 10%. The quantum yield determinations were carried out in a room with dim red lights.

The amounts of reactant decomposed in the reaction was determined spectrally by recording the decrease in the absorption of the charge-transfer bands. The Beer–Lambert law was obeyed by all complexes used in this study. The absorption maximum and molar extinction coefficients of the charge-transfer band for the chelates in absolute ethanol are: Cu(acac)$_2$, 245 nm, 1.48 × 10^4 l./(mol cm); Cu(tfac)$_2$, 238 nm, 1.10 × 10^4 l./(mol cm); Cu(hfac)$_2$, 228 nm, 8.52 × 10^3 l./(mol cm); Cu(t-buac)$_2$, 246 nm, 1.43 × 10^4 l./(mol cm); Cu(bzac)$_2$, 256 nm, 2.52 × 10^4 l./(mol cm). The change in absorbance of the charge-transfer band, corrected for the absorbance due to the copper deposit, was compared to a Beer–Lambert law plot of the various chelates and the number of moles of reactant consumed in a given time was determined. This rate of decomposition was converted to molecules/sec, R_d.

The incident light intensity within the photolysis cell window, I_i^0, was determined by ferric oxalate actinometry. However, one of the products of the photoreduction, metallic Cu(0) which plates out on the front cell window, has the effect of a neutral density filter.[13] Thus as the photolysis proceeds, I_i^0 decreases. The growth of the optical density due to the copper deposit is approximately linear with time. From the Beer–Lambert law[15] the incident intensity at the end of the photolysis can be calculated from the expression

$$I_i^f = \frac{I_i^0}{\text{antilog }(A)} \qquad \text{(I)}$$

where I_i^f is the final incident intensity within the cell and A is the absorbance of the deposited copper film at 254 nm. The absorbance of the deposited copper film was determined after each photolysis by disconnecting the photolysis cell and rinsing the film and cell with absolute ethanol five times. The cell was then filled with absolute ethanol and the absorbance measured relative to a quartz reference cell filled with absolute ethanol. The mean incident intensity[16] $\{(I_i^0)(I_i^f)\}^{1/2}$ was used to calculate the quantum yield, *i.e.*

$$\Phi = R_d/\{(I_i^0)(I_i^f)\}^{1/2} \qquad \text{(II)}$$

In the case of optically dilute solutions the absorbed intensity, I_A, was determined by

$$I_A = \{(I_i^0)(I_i^f)\}^{1/2}(1 - e^{-A'}) \qquad \text{(III)}$$

where A' is the mean absorbance of the chelate at 254 nm computed from the absorbance measured before and after each photolysis and corrected for absorbance due to the copper film.

As stated above, about 90% of the lamp ouput is at 2537 Å. Most of the remaining 10% is contributed by the 1850-Å line. Photolysis through this line is not considered in the following discussion, since most of it is absorbed by the air gap between the lamp and the cell.

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(8) J. P. Fackler and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).

(9) J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1220 (1944).

(10) The authors thank R. F. Handy for the sample of bis(1-phenyl-1,3-butanedionato)copper(II).

(11) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **5**, 489 (1966).

(12) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953).

(13) C. G. Hatchard and C. A. Parker, *ibid., Ser. A*, **235**, 518 (1956).

(14) C. A. Parker, *Trans. Faraday Soc.*, 50, 1213 (1954).

(15) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 1.

(16) W. A. Noyes and P. A. Leighton, "Photochemistry of Gases," Reinhold, New York, N. Y., 1941, Chapter 4.

Table I. Material Balance for Moles of Cu(II) Consumed and Moles of Cu(0) Produced during the Photolysis of $Cu(tfac)_2$

Sample no.	Initial [chelate]	No. of moles of $Cu(tfac)_2$ remaining	No. of moles consumed	No. of moles of Cu(0) produced	Moles of Cu(0) produced/moles of $Cu(tfac)_2$ consumed
1	1.0×10^{-4}	2.76×10^{-7}	2.48×10^{-7}	2.79×10^{-7}	1.1
2	1.0×10^{-4}	2.40×10^{-7}	2.84×10^{-7}	2.38×10^{-7}	1.2
3	1.0×10^{-4}	3.66×10^{-7}	1.58×10^{-7}	1.50×10^{-7}	0.9
4	1.0×10^{-4}	3.70×10^{-7}	1.54×10^{-7}	1.72×10^{-7}	1.1
5	1.0×10^{-3}	3.87×10^{-7}	5.00×10^{-7}	5.85×10^{-7}	1.2

Results

Preliminary experiments indicated that the reaction is dependent upon the presence of oxygen. The photolysis of solutions open to the atmosphere resulted in a change from the initial blue-green color of the solution to a colorless solution with a dispersed black solid containing copper and a metallic copper film on the quartz immersion well. However, the amount of the black solid varied in different experiments conducted under the same conditions. Aliquots of the photolyzed solution quickly reverted back to the initial blue-green color when removed from the reaction vessel. The photochromic behavior of the system was demonstrated by repeated photolyses of the same solution of $Cu(acac)_2$ in absolute ethanol. The solution was irradiated for 1–3 hr, allowed to sit overnight, and then irradiated again the following day. Three consecutive irradiations were carried out in this manner. On the third photolysis a green gelatinous solid precipitated from the solution. This was isolated and dried by vacuum filtration. It decomposes at 230°. The infrared spectrum and analysis indicate copper acetate. The protonated form of the ligand was also isolated by vacuum distillation and identified spectrally. Resistance measurements made during the photolysis showed 620×10^2 and 490×10^2 ohm decreases for ethanol solutions of $Cu(tfac)_2$ and $Cu(acac)_2$, respectively.

In the absence of air the reactions are not reversible. Under these conditions, no black solid is present and there is no change in the resistance of the solutions throughout the photolysis.

The products of the reaction in the absence of oxygen were isolated by vacuum distillation. The ultraviolet and infrared spectra of the distillate proved that one of the products was the protonated form of the ligand. The amount of the other major product, metallic copper, was determined by atomic absorption spectroscopy. The results for a series of $Cu(tfac)_2$ solutions are given in Table I. Similar determinations for $Cu(acac)_2$ resulted in a molar ratio of 0.9 ± 0.2. Thus the overall reaction in the absence of air can be written as

$$CuL_2 \xrightarrow[\text{EtOH}]{h\nu} Cu + 2HL$$

No attempt was made to quantitatively determine the amount of protonated ligand produced because ethanolic solutions of pure trifluoroacetylacetone decompose when exposed to 254-nm radiation.

Successive recordings of the absorption spectra of degassed 10^{-4} *M* chelate solutions for various irradiation times indicated that the photoreduction up to 45–55% consumption of the reactant could be followed by measuring the decrease in the absorbance of the charge-transfer bands. In general, 10–40% of the reactant was consumed in a given photolysis.

The rate of photoreduction was studied as a function of the initial concentration of the chelate from 10^{-6} to 5×10^{-3} *M*. Limited solubility at low temperatures required a somewhat lower maximum concentration (*ca.* 3×10^{-3} *M*) for $Cu(acac)_2$ and $Cu(bzac)_2$. Solutions of low concentration with absorbances of less than 1.0 at 254 nm obey a first-order rate law. Solutions of higher concentration and absorbances greater than 10.0 are zero order in chelate concentration. Figure 1, a plot of the integrated first-order rate equation, shows that the reactions have a short induction time.[17] The induction times varied from 1 to 3 min for concentrated solutions to *ca.* 8 min for dilute solutions.

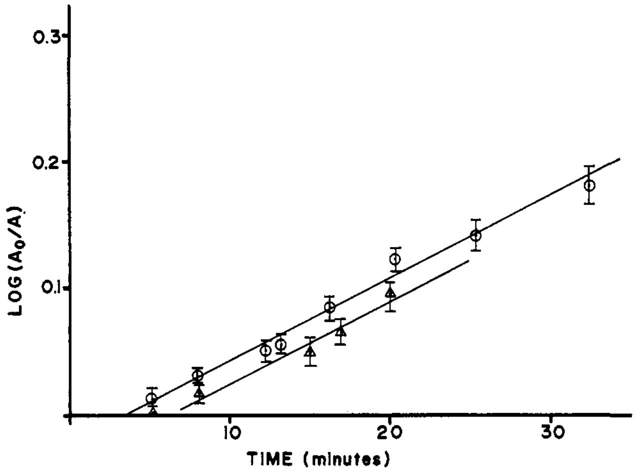

Figure 1. Plot of integrated first-order rate equation for decomposition of $Cu(tfac)_2$ in ethanol: ○, 6.4×10^{-5} *M* $Cu(tfac)_2$; △, 3.2×10^{-5} *M* $Cu(tfac)_2$. Average intensity *ca.* 2.0×10^{15} quanta/sec, temperature *ca.* 28°.

The light intensity dependence was determined by irradiating 10^{-3} *M* solutions of the various chelates. The results for $Cu(tfac)_2$ are shown in Figure 2. The resulting straight line has a slope of 0.9 ± 0.1. Thus the rate equation for optically dense solutions can be written as

$$-\frac{\Delta(CuL_2)}{\Delta t} = \Phi I^1 \qquad \text{(IV)}$$

The quantum yield at 254 nm for photolysis of the various chelates in absolute ethanol are summarized in Table II. The results obtained with solutions degassed by the freeze–thaw technique show excellent agreement

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[17] S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 53.

Table II. Quantum Yields for Reduction of Cu(1,3-diketonate)$_2$ Chelates[a]

Compound	Initial concn, M	Intensity, quanta/sec	Reaction rate, molecules/sec	Φ_{av}[c]
Cu(acac)$_2$	1.0×10^{-3}	3.23×10^{15}	4.52×10^{13}	0.018 ± 0.005
	4.26×10^{-5}	3.09×10^{15} [b]	1.97×10^{13}	0.017 ± 0.004
Cu(tfac)$_2$	1.0×10^{-3}	3.40×10^{15}	6.97×10^{13}	0.027 ± 0.007
	6.0×10^{-5}	3.35×10^{15} [b]	2.90×10^{13}	0.028 ± 0.004
Cu(hfac)$_2$	1.0×10^{-3}	2.99×10^{15}	1.04×10^{14}	0.036 ± 0.006
	5.95×10^{-5}	3.79×10^{15} [b]	3.23×10^{13}	0.034 ± 0.005
Cu(t-buac)$_2$	1.0×10^{-3}	4.30×10^{15}	5.16×10^{13}	0.012 ± 0.004
	6.50×10^{-5}	4.83×10^{15} [b]	2.83×10^{13}	0.012 ± 0.001
Cu(bzac)$_2$	1.0×10^{-3}	4.11×10^{15}	7.36×10^{13}	0.018 ± 0.004
	6.50×10^{-5}	4.58×10^{15} [b]	4.47×10^{13}	0.017 ± 0.003

[a] Results obtained at 27 ± 1°. [b] Measured intensity, must be corrected for the fraction of light absorbed by eq III. [c] The quantum yields shown are computed by eq II. Each value is the result of at least 4 and as many as 12 independent determinations.

between values obtained with optically dense solutions (absorbance greater than 10) and optically dilute solutions (absorbance less than 0.8).

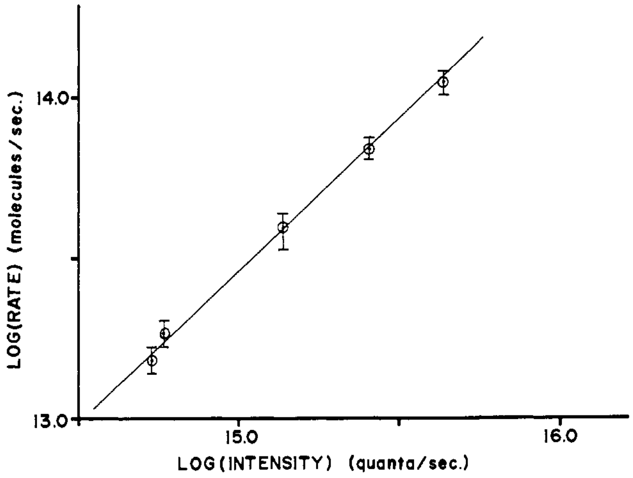

Figure 2. Plot of log R_d vs. log I for irradiation of Cu(tfac)$_2$ at 254 nm.

The wavelength dependence of the quantum yield was determined by irradiating ethanol solutions of the chelates. This Hg line was isolated by filtering with Corex glass which has 0% T at wavelengths shorter than 260 nm. The degassed solutions showed no detectable photochemical reaction when irradiated for 3-5 hr.

The effect of oxygen on the photoreduction is pronounced. Ethanol solutions of Cu(tfac)$_2$ irradiated while air was bubbled through the solutions showed no observable product. The quantum yield of a sealed 1.29×10^{-4} M solution of Cu(tfac)$_2$ in ethanol containing dissolved air is 1.3×10^{-3}. This corresponds to a 95% decrease in the quantum yield compared to degassed solutions.

Since qualitative experiments indicated a temperature dependence for all chelates, the effect of temperature on the quantum yield for Cu(tfac)$_2$ was determined. From Table II, the quantum yield at 26° is 0.028 ± 0.004, while at 3° the quantum yield was found to be 0.011 ± 0.002. Thus, ethanol solutions of this chelate showed a 41% decrease in quantum yield on lowering the temperature 23°. We also observed a slight increase in the induction time.

The solvent dependence of the reaction was investigated by irradiation of 10^{-3} M Cu(tfac)$_2$ in various alcohols. The resulting average quantum yields increased in the order methanol < ethanol $\lesssim$ 1-propanol. The photoreduction was also found to occur in chloroform. However, the resulting product appears to be a polymeric cuprous chloride salt, containing 56.3% Cu, 28.8% Cl, and small amounts of carbon and oxygen. It is known that chloroform undergoes a photodecomposition with the production of chlorine atoms.[18] The observed reaction may result from these atoms attacking the reactant or metallic copper.

The photoreduction of ethanol solutions of Cu(tfac)$_2$ was found to be independent of changes in the ionic strength. The quantum yield did not change in solutions containing 5.9×10^{-2} M lithium chloride. However, the effect of water on the quantum yield varies in a manner that is dependent upon the ligand substituents. These results are shown in Table III.

Table III. Effect of Water on the Quantum Yields

Compound	Initial concn, M	[H$_2$O], M	Φ[a]
Cu(acac)$_2$	6.63×10^{-5}	6.50×10^{-2}	0.018 ± 0.003
Cu(tfac)$_2$	7.02×10^{-5}	6.50×10^{-2}	0.016 ± 0.004
Cu(hfac)$_2$	6.70×10^{-5}	6.50×10^{-2}	0.053 ± 0.009

[a] Quantum yields determined at 24 ± 1°.

Discussion

Several experimental observations are explained by the reaction scheme shown below.

$$\mathrm{CuL_2} + h\nu \xrightarrow[k_{-1}]{k_1} [\mathrm{CuL \cdot L}]^* \qquad \text{(V)}$$

$$[\mathrm{CuL \cdot L}]^* \xrightarrow{k_2} \mathrm{CuL} + \mathrm{L\cdot} \qquad \text{(VI)}$$

$$\mathrm{CuL} \xrightarrow{k_3} \mathrm{Cu^0} + \mathrm{L\cdot} \qquad \text{(VII)}$$

The constants k_1, k_{-1}, and k_2 are the rate constants of excitation, radiationless deactivation, and diffusion from the solvent cage. In addition to metallic copper, the protonated ligand has been isolated and identified as a product of the photolysis. Thus, an additional reaction involving hydrogen atom abstraction from the solvent by the ligand radicals is taking place.

The kinetic studies show that the rate law for photodecomposition of CuL$_2$ (eq V and VI) is independent of chelate concentration and has a first-order dependence

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(18) J. P. Simons and A. J. Yarwood, *Trans. Faraday Soc.*, 57, 2167 (1961).

on light intensity (eq IV). Such kinetic behavior is consistent with a primary photochemical process. In optically dense solutions, the rate of disappearance of the chelate is given by

$$\frac{-\Delta \mathrm{CuL}_2}{\Delta t} = \left(1 - \frac{k_{-1}}{k_2 + k_{-1}}\right) I \qquad \text{(VIII)}$$

Comparison of eq VIII with eq IV and rearranging yields

$$k_2/k_{-1} = \Phi/(1 - \Phi)$$

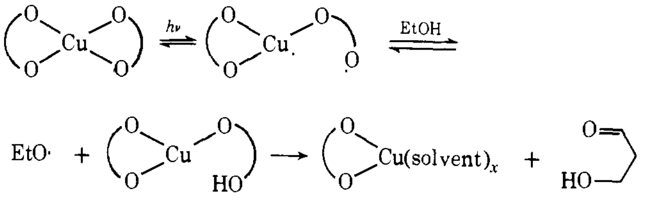
The rate constant k_2 can be estimated from the lifetime of the excited state $[\mathrm{CuL \cdot L}]^*$. The lifetimes of excited states were calculated by the method of Strickler and Berg[19] from a Gaussian analysis of the charge-transfer bands. The results indicate lifetimes from 0.7×10^{-9} to 2.0×10^{9} sec. For $\mathrm{Cu(tfac)_2}$ the lifetime is *ca.* 1×10^{9} sec. Therefore, $k_2 \geqslant 1 \times 10^{9}\ \mathrm{sec}^{-1}$ and $k_{-1} \geqslant 3 \times 10^{10}\ \mathrm{sec}^{-1}$. We were unable to observe emission from ethanol solutions of these chelates either at room temperature or at 77°K.

The mechanism for the photoreduction proposed above involves a Cu(I) intermediate which decomposes thermally to metallic copper, eq VII. Experimentally, this is supported by two independent observations. First, the quantum yield is temperature dependent. No temperature dependence is expected for the first reduction step, eq V and VI, since it is a primary process.[20] However, if the final step, eq VII, is a thermal reaction, the overall process would be temperature dependent. In addition, it is very unlikely that the reaction Cu(I) → Cu(0) is photochemically induced, since it is observed under conditions where essentially all of the light is being absorbed by the Cu(II) chelate. Second, a reactive, black copper-containing intermediate appears during the photolyses. This may well be the Cu(I) intermediate, since Nast[21] has reported the preparation and characterization of a black Cu(I) acetylacetonate which readily decomposes to metallic copper and $\mathrm{Cu(acac)_2}$.

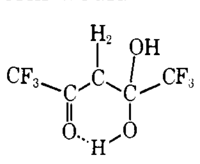
Besides these experimental observations, a one-step two-electron photoreduction would not be expected to be important since the spectral transition is highly forbidden. Thus, our data and observations are best explained by a primary photoreduction of the chelated Cu(II) to a Cu(I) intermediate. The Cu(I) intermediate then undergoes a thermal reduction to Cu(0).

The mechanism of the thermal reduction of the Cu(I) species is not known. However, the induction time observed, Figure 1, supports a disproportionation reaction, $2\mathrm{CuL} \rightarrow \mathrm{Cu} + \mathrm{CuL_2}$. The induction time is the time required to produce a steady-state concentration of the intermediate. Rapid reduction of Cu(I) species is expected since Cu(I) is not stable in either ethanol or acetylacetone.[22]

The proposed mechanism involves the free-radical dissociation of the ligand followed by hydrogen atom abstraction. Several independent experiments support this mechanism. First, the resistance of the solutions is constant during the course of the reaction, indicating no appreciable concentration of charged species. Second, the quantum yields are independent of changes in ionic strength. This is expected for a reaction involving uncharged species. Third, the quantum yield in different alcohols increases in the order $\mathrm{CH_3OH} < \mathrm{C_2H_5OH} \leqslant n\text{-}\mathrm{C_3H_7OH}$. Thus, as the heat of formation of the solvent radical decreases the quantum yield increases. This behavior is typical of a radical reaction.[23] Fourth, the overall reduction is temperature dependent, indicating that there are thermal as well as photochemical reactions. The approximate activation energy calculated from the results of the temperature studies is 65 cal/mol. This very low activation energy is consistent with a mechanism in which hydrogen atom abstraction by the ligand radical is the rate determining step.[24] The proposed mechanism for the reduction to a Cu(I) species is shown below.



In order to determine the effect of water on the photoreduction, the quantum yields for three chelates were measured in ethanol–water mixtures. The results presented in Table III show that the effect of water on the quantum yield depends upon the ligand. If the only effect of water was due to interaction with the fifth and sixth coordination sites on Cu(II), similar effects would be expected for all chelates. Clearly, this is not the case. The quantum yield for $\mathrm{Cu(acac)_2}$ is not changed by the presence of water, while it is decreased for $\mathrm{Cu(tfac)_2}$ and increased for $\mathrm{Cu(hfac)_2}$. The results for $\mathrm{Cu(acac)_2}$ and $\mathrm{Cu(tfac)_2}$ might be expected since strong hydrogen bonds between fluorine and water offer an efficient mechanism for loss of exciting energy into the solvent. The result of this interaction is an increase in k_{-1} and a decrease in the quantum yield of reduction for $\mathrm{Cu(tfac)_2}$. However, this cannot explain the reaction of $\mathrm{Cu(hfac)_2}$ in the presence of water since the quantum yield of reduction for $\mathrm{Cu(hfac)_2}$ increases with the addition of water. Chelates containing this ligand are, in general, unstable in the presence of water. Belford, Martell, and Calvin[25] have reported that the chelated ligand hydrolyzes without any change in the absorption spectra. The hydrolyzed chelate can be isolated and even sublimed without loss of water.[11] The anhydrous chelate can only be recovered under rigorous drying conditions. Thus, it is likely that in the presence of water, a hydrolyzed molecule is being photolyzed. Belford, Martell, and Calvin[25] have suggested that the ligand hydrolyzes to the alcoholic ketone shown in **1**. The ligand in this form would be expected to have an



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(19) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37, 814 (1962). We have assumed emission and absorption at the same wavelength for all chelates.

(20) Reference 15, p 646.

(21) R. Nast, R. Mohr, and C. Schultz, *Chem. Ber.*, 96, 2127 (1963).

(22) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, 22, 279 (1961).

(23) I. P. Gray and A. Williams, *Chem. Rev.*, 59, 239 (1959).

(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1965, p 108.

(25) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, 2, 11 (1956).

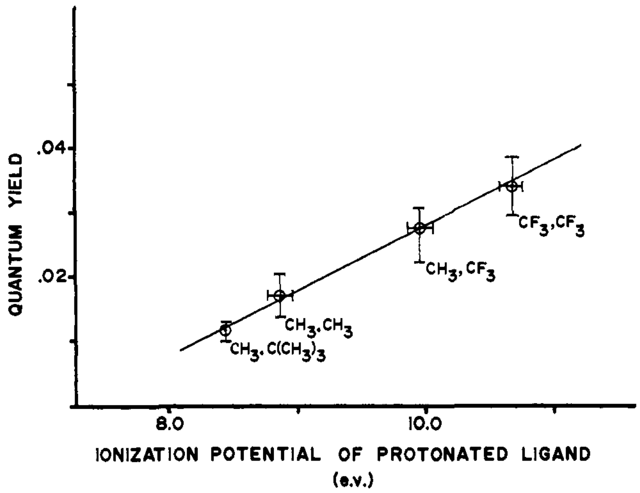

Figure 3. Ionization potentials of the protonated ligand *vs.* the quantum yield for reduction of Cu(1,3-diketonates)$_2$ irradiated at 254 nm.

enhanced inductive effect due to the presence of the hydroxyl group. The data plotted in Figure 3 show that strong electron withdrawal by induction results in a large quantum yield. Therefore, the increase in the quantum yield for Cu(hfac)$_2$ in the presence of water is attributed to hydrolysis of the chelated ligands.

Wavelength-dependent photoredox experiments are potentially useful in the study of charge-transfer spectra. The qualitative model for charge-transfer transitions treats the charge-transfer excited state as oxidized and reduced species.[26] The direction of the charge transfer can be either ligand-to-metal or metal-to-ligand. Irradiation of specific bands followed by isolation of oxidized and reduced species lends strong experimental support to the spectral assignments. In this manner, the assignment of the 230–255-nm band to a ligand-to-metal charge transfer, originally made by Fackler, Cotton, and Barnum,[7] is substantiated by this study. Isolation of reduced copper produced in a primary photochemical process at 2537 Å proves that the spectral band is due to a ligand-to-metal charge-transfer transition. The large molar extinction coefficient, *ca.* 10^4 l./(mol cm), and short lifetimes, *ca.* 10^{-9} sec, indicate that the spin of the complex is not changed during the electron transfer. The band position is insensitive to polar solvents and dissolved anions, indicating that the acceptor orbital is the σ antibonding $d_{x^2-y^2}$ orbital. Thus, the excited state contains a longer and weaker metal–ligand bond than the ground state and undergoes a facile loss of the ligand radical. The insensitivity of the quantum yields to changes in ionic strength indicates that the excited state formed is not charged or polarized to any significant extent.[27] The wavelength dependence of the quantum yield, *i.e.*, zero at 312 nm and in the visible, indicates that the reaction occurs only from the charge-transfer state and is not the result of chemical changes induced in the ligands. It is interesting to note that in the cases where the charge-transfer transitions occur at energies lower than ligand excited states,[3,4] reduction occurs from both the charge-transfer and ligand excited states. In the case of Cu(II) 1,3-diketonates, where the charge-transfer transitions are higher in energy than the ligand excited states, reduction occurs only from the charge-transfer state.

The values of the quantum yields as a function of the 1,3 substituents are of interest in assessing the influence of electronic effects on the photochemical reduction. The variation of quantum yield with different substituents cannot be accounted for by differences in the lifetimes of the excited states. Lifetimes calculated from the absorption spectra indicate that the reactivity should be in opposite order of that observed. The position of the charge-transfer band relative to the exciting wavelength differs with various 1,3 substituents. This results in different fractions of the radiation absorbed. In all cases, more than 80% of the radiation is absorbed by the charge-transfer band. If the fraction of 2537-Å light absorbed were the determining factor, the quantum yield would be largest for Cu(bzac)$_2$ and smallest for Cu(hfac)$_2$. The opposite is true. The variation in the quantum yields can be explained if one considers the excited states involved. The photoinduced transfer of the electron can be considered as ionization of the ligand. Several ionization potentials for 1,3-diketones have been measured.[28] The ionization potential of 2,2-dimethyl-3,5-hexanedione was estimated from a plot of the ionization potential of the protonated ligand *vs.* the average ionization potential of the substituents. The value calculated agrees well with the value estimated from the data of Holtzclaw.[29]

In Figure 3, ionization potentials are plotted *vs.* the quantum yields of decomposition. The ligands are identified in the figure by the groups substituted in the 1 and 3 positions. Figure 3 shows a linear dependence between the ionization potential of the ligand and the quantum yield for the corresponding chelate. As the ionization potential of the ligand increases, the quantum yield of decomposition increases also. A mechanism in which the rate-determining step is hydrogen atom abstraction from the solvent by the ligand radical is consistent with all the data. The fluorinated ligands have the largest ionization potentials and would therefore release the most energy upon abstraction of a hydrogen atom from the solvent.

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(26) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, Chapter 7.

(27) Reference 24, pp 150–157.

(28) S. M. Schildcrout, R. G. Pearson, and F. E. Stafford, *J. Amer. Chem. Soc.*, **90**, 4006 (1968).

(29) H. F. Holtzclaw, R. L. Lintvedt, H. E. Baumgarten, R. G. Parker, M. M. Bursey, and P. F. Rogerson, *ibid.*, **91**, 3774 (1969).